Production and verification of stoichiometric uranium dioxide

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SCK•CEN mentors: Prof. Dr. T. Cardinaels & Dr. M. Verwerft

Overview

- Scope of the study
- Background
- Production of stoichiometric UO_2
- Verification of stoichiometry
- Conclusions

Overview

- **Scope of the study**

  Accurate lattice parameter measurement of stoichiometric UO_2

- Background

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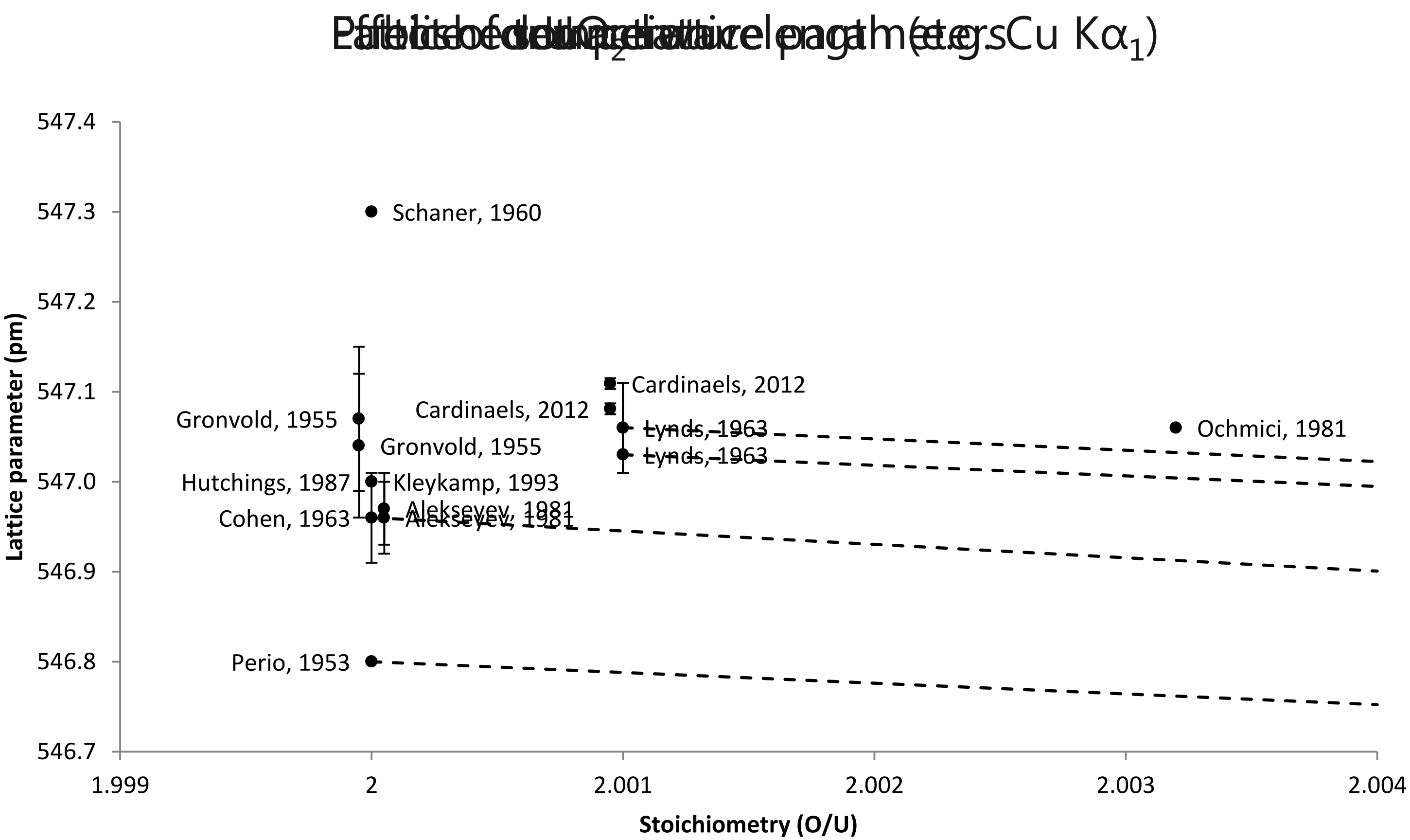
Context: UO_2 lattice parameter



Overview of published UO_2 lattice parameters

Context: UO_2 lattice parameter

Objectives:

- Produce a stoichiometric UO_2 sample suitable for analysis
- Accurately measure the lattice parameter
- Accurately measure sample stoichiometry

Context: UO_2 lattice parameter

Objectives:

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Which parameters control deviation from stoichiometry?

How to prepare a stoichiometric sample?

How to accurately measure (verify) sample stoichiometry?

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U-O chemistry

UO_2 production

Ideally: Reduction of U_3O_8 to UO_2

$$\mathrm{U_3O_8 + 2H_2 \rightarrow 3UO_2 + 2H_2O}$$

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Reality: oxidation, even at room temperature

$$UO_2 + \frac{x}{2}O_2 \rightarrow UO_{2+x}$$

UO_{2+x} powder

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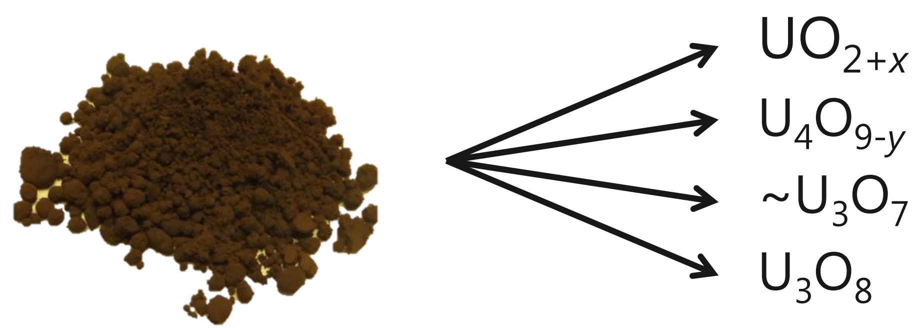

UO_{2+x} powder

Question (1/3)

Which parameters control deviation from stoichiometry?

Two stage reaction (1/2)

Low temperature oxidation reaction (T < 200 °C)

$$\mathbf{UO_2} + \frac{\boldsymbol{x}}{\mathbf{2}}\mathbf{O_2} \rightarrow \mathbf{UO_{2+\boldsymbol{x}}}$$

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Low temperature oxidation reaction (T < 200 °C)

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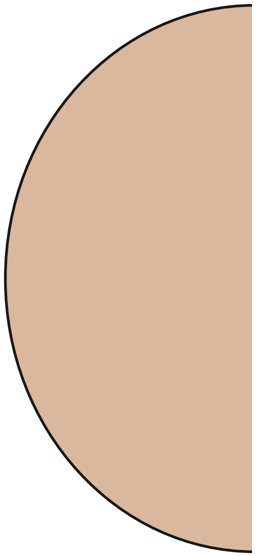
→ Chemi- and physisorption of O_2 on surface of UO_2 grains



O_2 molecules **UO_2 grain**

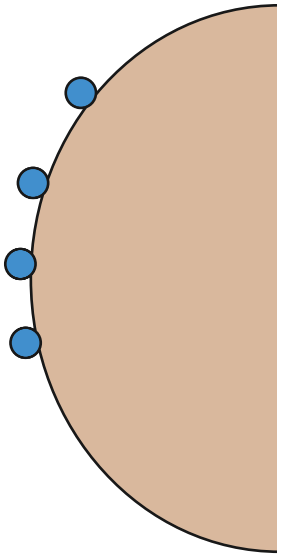
Two stage reaction (2/2)

Low temperature oxidation reaction (T < 200 °C)

$$\mathbf{UO_2 + \frac{x}{2} O_2 \rightarrow UO_{2+x}}$$

→ Chemi- and physisorption of O_2 on surface of UO_2 grains
→ Diffusion of oxygen into the bulk

Availability of oxygen
Reactivity of powder



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Controlling stoichiometry deviation (1/3)

Approach: Inert atmosphere

→ Decrease availability of oxygen

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Requires large facility with multiple glove boxes

Glove box facilities at SCK•CEN laboratories

Controlling stoichiometry deviation (1/3)

Approach: Inert atmosphere

→ Decrease availability of oxygen

Requires large facility with multiple glove boxes

Sample preparation ✓

Sample analysis ✗

Stoichiometry ✓

Glove box facilities at SCK•CEN laboratories

Controlling stoichiometry deviation (2/3)

Approach: Inert atmosphere

→ **Route abandoned**

Approach: Coarse grained powder

→ Decrease reactivity of powder

Controlling stoichiometry deviation (2/3)

Approach: Coarse grained powder

→ Decrease reactivity of powder

Ideally: Reduction of U_3O_8 to UO_2

$$U_3O_8 + 2H_2 \rightarrow 3UO_2 + 2H_2O$$

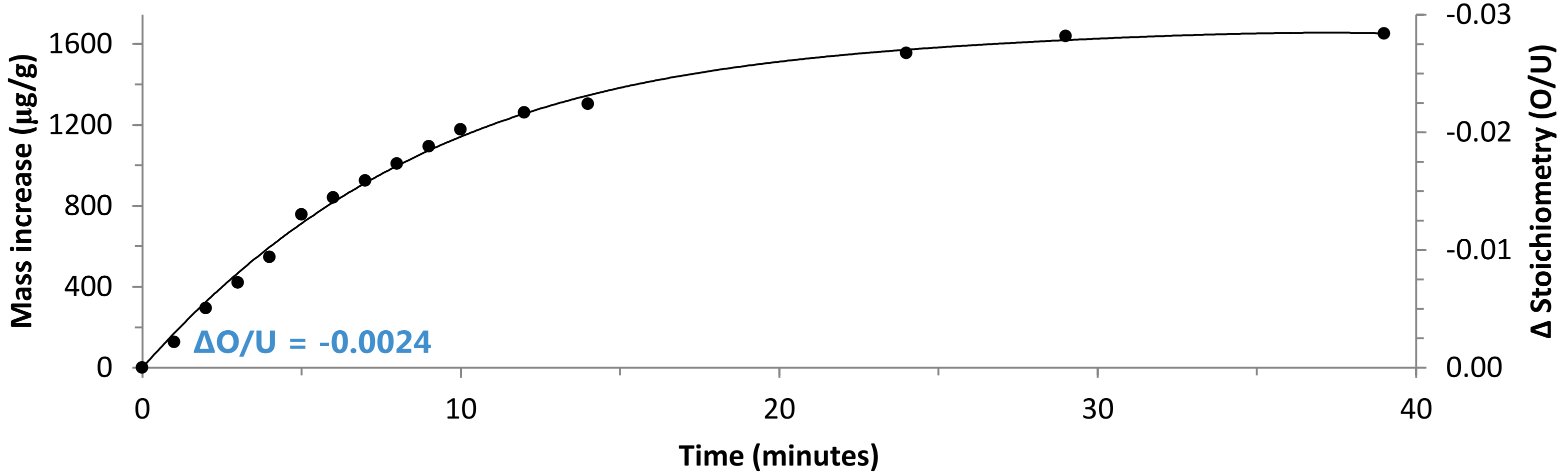
Controlling stoichiometry deviation (2/3)

Approach: Coarse grained powder

→ Decrease reactivity of powder

Ideally: Reduction of U_3O_8 to UO_2

Reality: oxidation to UO_{2+x} ✘



Measured mass increase in prepared coarse UO_2 powder upon exposure to lab environment

Controlling stoichiometry deviation (3/3)

Approach: Inert atmosphere

→ **Route abandoned**

Approach: Coarse grained powder

→ **Route abandoned**

Approach: Sintered UO_2 pellet, theoretical density > 95 %

→ Further decrease reactivity of powder

Controlling stoichiometry deviation (3/3)

Approach: Sintered UO_2 pellet, theoretical density > 95 %

→ Further decrease reactivity of powder

Properties:

- No open porosity, S.A. << 1 $m^2\ g^{-1}$
- Large, polycrystalline compact body
- Stoichiometry close to $UO_{2.000}$

Sintered UO_2 pellet

Controlling stoichiometry deviation (3/3)

Approach: Sintered UO_2 pellet, theoretical density > 95 %

→ Further decrease reactivity of powder

Properties:

- No open porosity, S.A. << 1 $m^2\ g^{-1}$
- Large, polycrystalline compact body
- Stoichiometry close to $UO_{2.000}$

No oxygen take-up witnessed after several weeks

Comparable state with real application: fuel pellet

Requires polishing (XRD sample)

Polished, imbedded UO_2 pellet

Question (2/3)

How to prepare a stoichiometric sample?

Controlling stoichiometry deviation (3/3)

Approach: Inert atmosphere

→ **Route abandoned**

Approach: Coarse grained powder

→ **Route abandoned**

Approach: Sintered UO_2 pellet

→ **Chosen route**

Sintering

Sintering: UO_{2+x} green pellets to $UO_{2.000}$

T_{sinter} = ± 1750 °C t_{dwell} = 8 h

- T.D. > 95 %

Atmosphere: reducing

- $\mu_{O2} \leq -420$ kJ mol^{-1} (at T_{sinter})

Sinter furnace

Sintering

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Atmosphere: reducing

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Sinter furnace

Accurate control of sintering atmosphere required

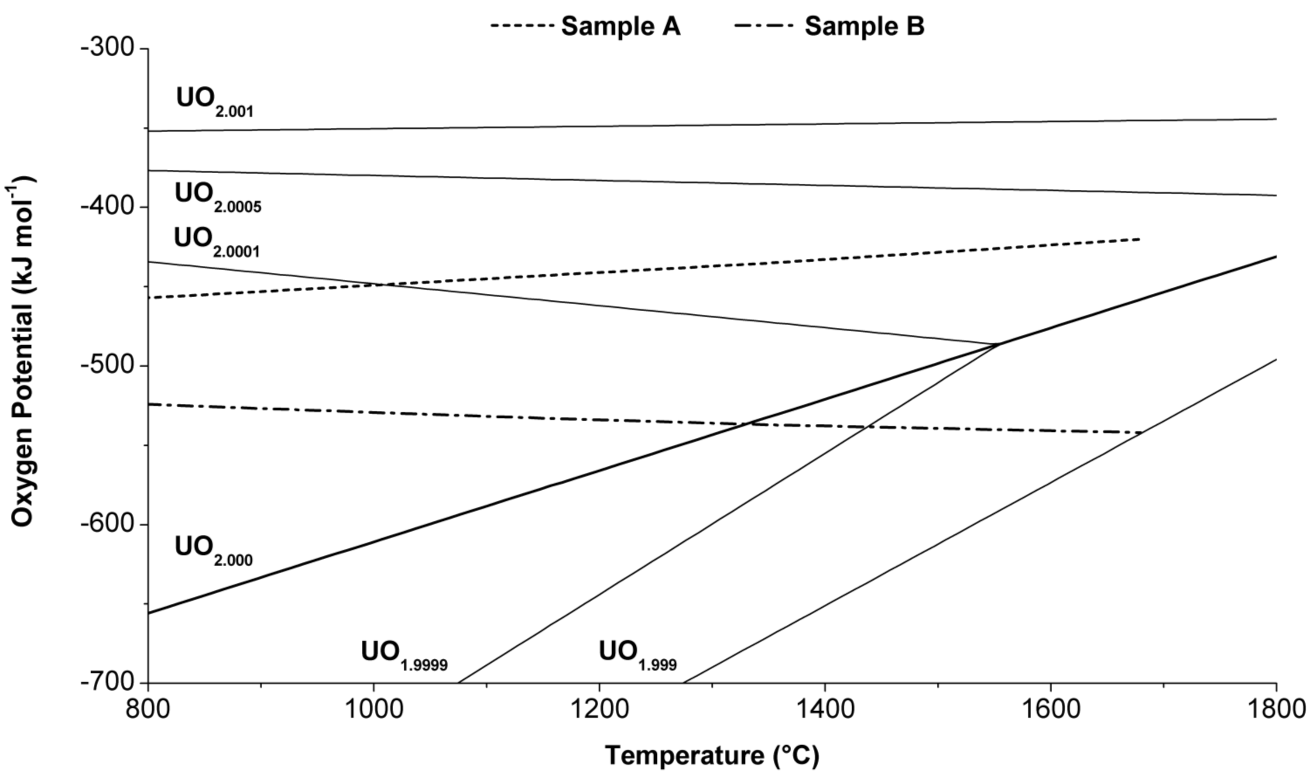
→ Mixing high purity gasses: H_2 + O_2 (in Ar)

$2H_2 + O_2 \rightarrow 2H_2O$ equilibrium reaction

Sintering atmosphere

Atmosphere: reducing

- $\mu_{O2} \leq$ -420 kJ mol^{-1} (at T_{sinter})



Ellingham diagram for $UO_{2\pm x}$

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- **Verification of stoichiometry**
  - **Ignition method with corrections**
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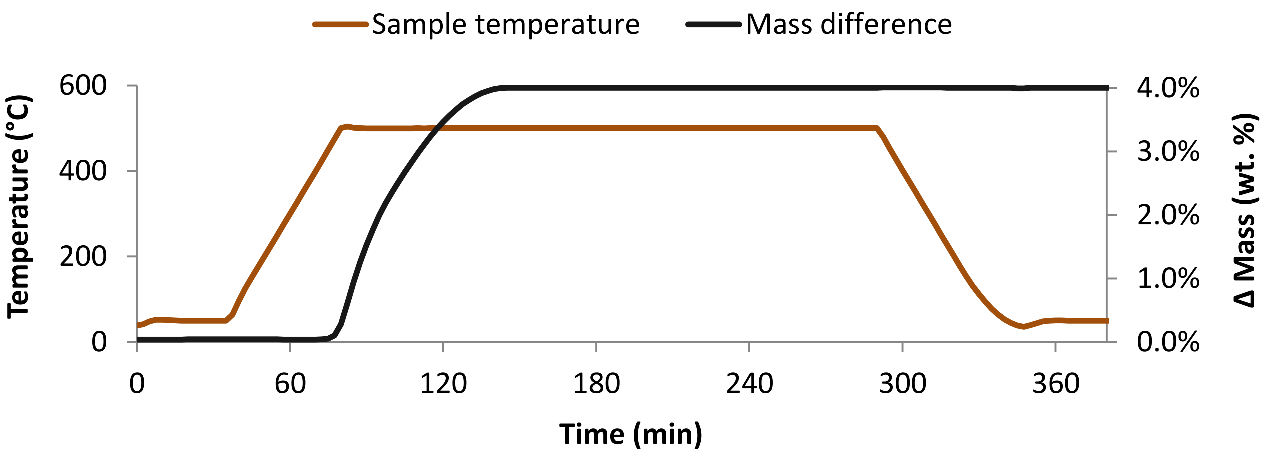
O/U measurement

Most commonly used method: mass difference after oxidation

$$3UO_{2+x} + \frac{1}{2}(2-3x)O_2 \rightarrow U_3O_8$$

Mass: y z



Thermogravimetric analysis to determine O/U ratio in sintered UO_2 pellets

O/U measurement

Most commonly used method: mass difference after oxidation

$$3UO_{2+x} + \frac{1}{2}(2 - 3x)O_2 \rightarrow U_3O_8$$

Mass: *y* *z*

Not as evident as it may seem

→ Requires high accuracy on mass signal: $y, z >> x$

Question (3/3)

How to accurately measure (verify) sample stoichiometry?

Ignition method

Main sources of error:

- Precision of the (micro-)balance

Ignition method

Main sources of error:

Precision of the (micro-)balance

→ The use of *in-situ* thermogravimetric analysis (TGA) can greatly improve the accuracy of the measurement

Ignition method

Main sources of error:

Precision of the (micro-)balance

Mass difference due to evaporation of volatile impurities

Ignition method

Main sources of error:

Precision of the (micro-)balance

Mass difference due to evaporation of volatile impurities

→ TGA + evolved gas analysis: no measurable volatiles from sintered pellet

↕

→ H_2O release from UO_{2+x} powder

Ignition method

Main sources of error:

- **Precision of the (micro-)balance**
- **Mass difference due to evaporation of volatile impurities**
- Mass difference due to reaction of impurities

Ignition method

Main sources of error:

Precision of the (micro-)balance

Mass difference due to evaporation of volatile impurities

Mass difference due to reaction of impurities

→ ICPMS analysis to evaluate impurity content

Stoichiometry measurements

Results:

- Initial mass: analytical balance (lab environment)
- Final mass: *ex-situ* (analytical balance)

  No correction for impurities

O/U (in-situ)		O/U (ex-situ)	
Correction	No correction	Corrected	No correction
			1.9934

Stoichiometry measurements

Results:

- Initial mass: analytical balance (lab environment)
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  Corrected for impurities

O/U (in-situ)		O/U (ex-situ)	
Correction	**No correction**	**Corrected**	**No correction**
		1.9955	1.9934

Stoichiometry measurements

Results:

- Initial mass: analytical balance (lab environment)
- Final mass: *in-situ* (TGA)

    No correction for impurities

O/U (in-situ)		O/U (ex-situ)	
Correction	**No correction**	**Corrected**	**No correction**
	1.9975	1.9955	1.9934

Stoichiometry measurements

Results:

- Initial mass: analytical balance (lab environment)
- Final mass: *in-situ* (TGA)

  Corrected for impurities

O/U (in-situ)		O/U (ex-situ)	
Correction	**No correction**	**Corrected**	**No correction**
1.9997 ± 0.0006	1.9975	1.9955	1.9934

Underestimation: adsorption

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Conclusions

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3 routes considered:

- **Inert atmosphere**
- **Coarse UO_2 powder**
- **Sintered UO_2 pellets**

Conclusions

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Conclusions

Objectives:

Produce a stoichiometric UO_2 sample suitable for analysis

Accurately measure the lattice parameter: completed

Accurately measure sample stoichiometry

Stoichiometry verification:

- **High accuracy via *in-situ* TGA ↔ *ex-situ* measurement**
- **No measurable volatile impurities on sintered pellets**
- **Corrected for the presence of impurities**

Conclusions: UO_2 lattice parameter

Overview of published UO_2 lattice parameters

G. Leinders, T. Cardinaels, K. Binnemans, M. Verwerft, *J. Nucl. Mater*. **2015**, *459*, 135.

Thanks for your attention

Gregory Leinders

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